Material and Energy Balances

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Lecture – 45
Fundamentals of Nonreactive Phase Change Processes

Welcome to todays lecture on non-reactive phase change process until the last class we have been looking at processes where there was no phase change. Today, we look at some of the fundamentals which are required for performing energy balance calculations for processes with phase change occurring.

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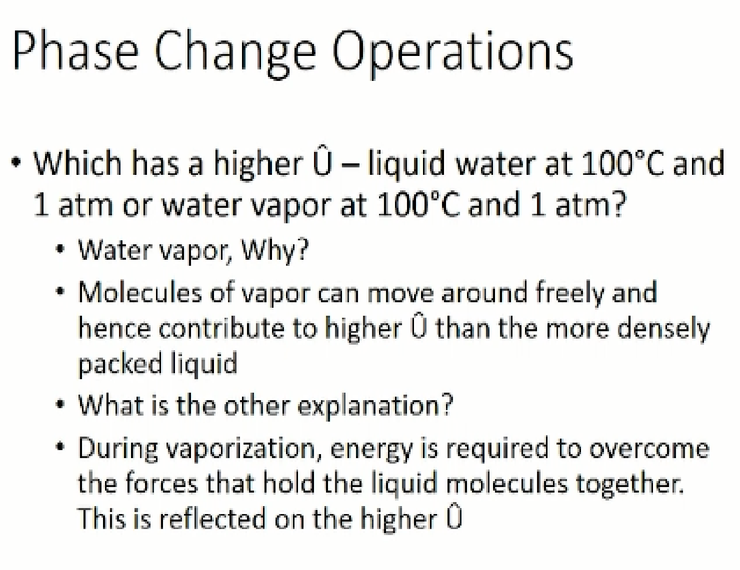

Phase Change Operations

- Which has a higher $\hat{U}$ – liquid water at 100°C and 1 atm or water vapor at 100°C and 1 atm?
  - Water vapor, Why?
  - Molecules of vapor can move around freely and hence contribute to higher $\hat{U}$ than the more densely packed liquid
  - What is the other explanation?
  - During vaporization, energy is required to overcome the forces that hold the liquid molecules together. This is reflected on the higher $\hat{U}$

Phase change operations are very common in any chemical or bio- chemical industry. So, you would have a change in enthalpy or internal energy associated with these phase changes which have to be accounted for when you perform energy balance calculations. Please look up the steam tables and answer this question which has higher specific internal liquid water at 100 degree Celsius at 1 atmosphere or water vapor at 100 degree Celsius at 1 atmosphere.

The answer is water vapor why you see that numerically this is higher but can you explain what the physical reason for this is molecules of a vapor can actually roam around more freely compared to the liquid hence it contributes to higher specific internal energy than the more densely packed liquids. So this is why you have a higher specific internal energy for water vapor.

What could be the other explanation? during vaporization energy is required to overcome the forces that are actually holding the molecules together in the liquid phase.

So, that it can actually become a vapor so the molecules which are held together in the liquid phase is the reason the liquid is maintaining its phase. So, for this phase to change from liquid to vapor these interactions would have to be broken and energy is supplied to the molecules for this to happen because these energies is absorbed by the liquid molecules and they convert to the vapor phase they have a higher internal energy.

And this is the reason we have higher internal energy for vapor phases compared to liquid.

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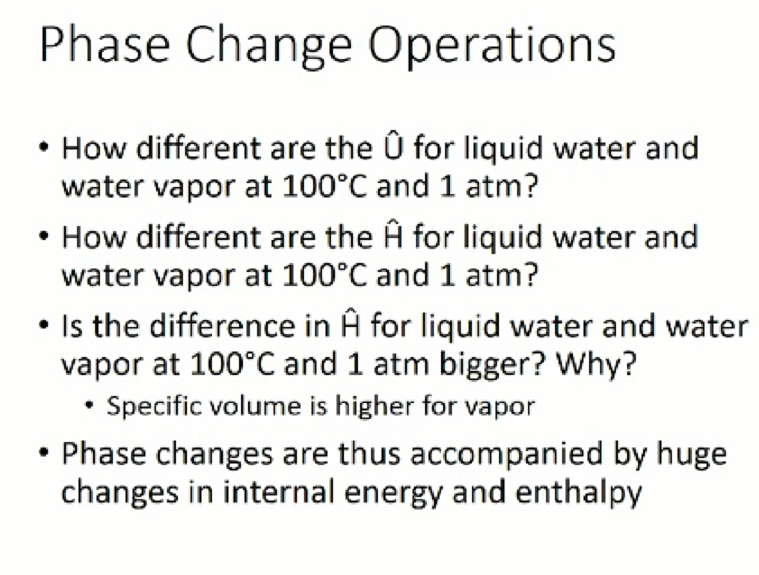

Phase Change Operations

- How different are the $\hat{U}$ for liquid water and water vapor at 100°C and 1 atm?
- How different are the $\hat{H}$ for liquid water and water vapor at 100°C and 1 atm?
- Is the difference in $\hat{H}$ for liquid water and water vapor at 100°C and 1 atm bigger? Why?
  - Specific volume is higher for vapor
- Phase changes are thus accompanied by huge changes in internal energy and enthalpy

When you compared the specific internal energy for liquid water and water vapor you saw that the specific internal energy for water vapor was higher. Now calculate the numerical difference between the specific internal energy of liquid water and water vapor at 100 degree Celsius at 1 atmosphere and do the same thing for specific enthalpy. Which of these is higher you would find that the specific enthalpy changes between the liquid and the vapor.

Is much higher than what you observe for the specific internal energy change this is because the specific volume is higher for vapor. As enthalpy accounts for internal energy and the PV cap term the value in difference would fall is higher for specific enthalpy compare to specific internal energy. Phase changes are thus accompanied by huge changes in internal energy and enthalpy and this has to be accounted for when we perform energy balance calculations.

So, it is important to understand the fundamentals associated with such process.

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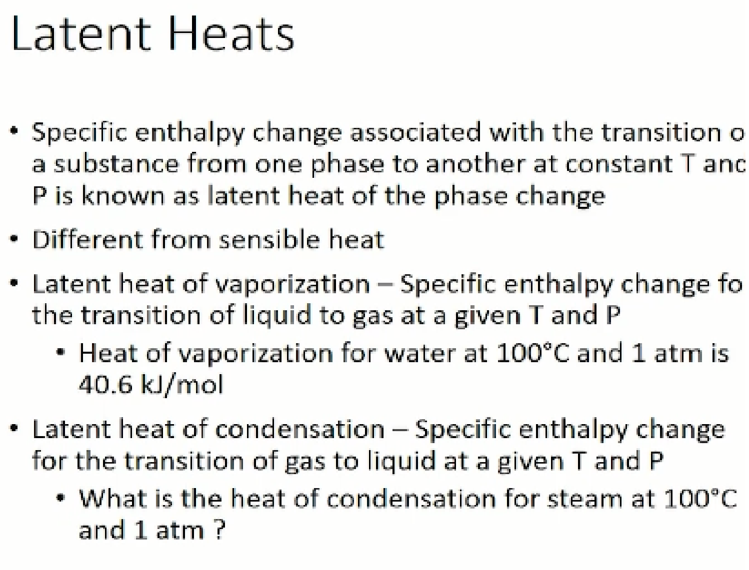

Latent Heats

- Specific enthalpy change associated with the transition o a substance from one phase to another at constant T anc P is known as latent heat of the phase change
- Different from sensible heat
- Latent heat of vaporization – Specific enthalpy change fo the transition of liquid to gas at a given T and P
    - Heat of vaporization for water at 100°C and 1 atm is 40.6 kJ/mol
- Latent heat of condensation – Specific enthalpy change for the transition of gas to liquid at a given T and P
    - What is the heat of condensation for steam at 100°C and 1 atm ?

The difference between the internal energy or enthalpy of the liquid phase and the gas phase or the solid phase and the liquid phase are due to something called as latent heat. So, we talked about sensible heat which is the heat which is taken up by a system to increase the temperature so that we have looked at earlier so what does latent heat. Here the heat supply does not help in increasing the temperature of the system.

However, it goes into changing the phase of the system so latent heat is specific enthalpy change associated with that transmission of a substance from one phase to another at constant temperature and pressure. So, this is also called as the latent heat of phase change you have different types of latent heats so this is different from the sensible heat sensible heat as I mentioned in helps in increasing the temperature.

Whereas latent heat helps in changing the phase. Latent heat of vaporization is the specific enthalpy change for transition of liquid to gas at given temperature and pressure so for water heat of vaporization at 100 degree Celsius and 1 atmosphere which is also called as the standard heat of the vaporization is 40.6 kilojoules for mol. Latent heat of condensation is the specific enthalpy change of transmission of gas to liquid at a given temperature and pressure.

Now that I have given you the heat of vaporization for water at 100 degrees Celsius in 1atmosphere can you identify what would be the heat of condensation of steam at 100 degree Celsius and1 atmosphere. The process is the reverse of the first process which means the heat associated enthalpy associated would be the negative of the value given so the heat of condensation would be negative of heat of vaporization.

So the numerical value for heat of condensation of steam would be -40.6 kilojoules per mol when the steam is condensing at 100 degrees Celsius and atmosphere.

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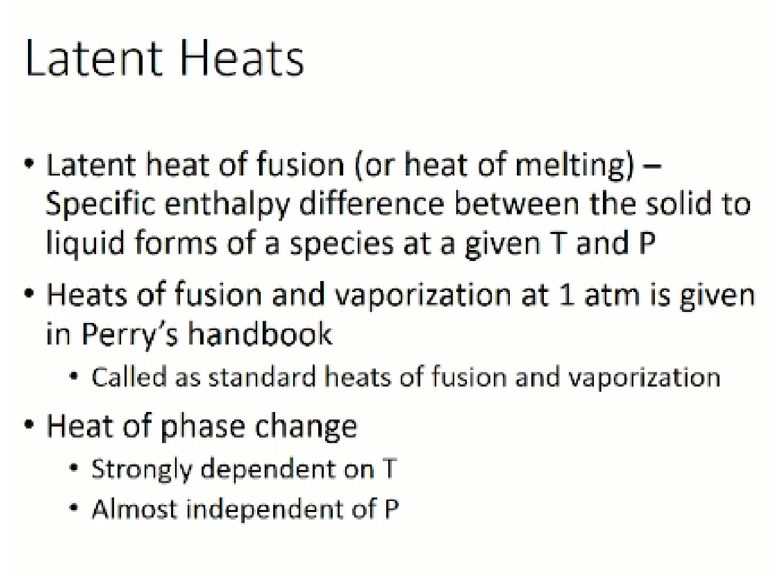

Latent Heats

- Latent heat of fusion (or heat of melting) – Specific enthalpy difference between the solid to liquid forms of a species at a given T and P
- Heats of fusion and vaporization at 1 atm is given in Perry's handbook
  - Called as standard heats of fusion and vaporization
- Heat of phase change
  - Strongly dependent on T
  - Almost independent of P

Latent heat of fusion or heat of melting is the specific enthalpy difference between the solid to the liquid forms of a species at given temperature and pressure. Heat of fusion and vaporization at one atmosphere is given in Perrys handbook and many other hand books or to even in some of the textbooks prescribed. These are called as the standard heats of fusion and vaporization these are commonly available for performing energy balance calculations.

Heat of phase change is strongly dependent on temperature and it is almost independent of pressure. So, depending on the temperature at which the phase change happens the heat of phase change would also be different. So the values we get directly from tables are usually the standard heat of vaporization and standard heat of fusion which means whenever we perform energy balance calculations the phase change happens at the specific boiling point.

Or melting point of the substance. So that way we can directly use the value from the table which would be the standard heat of phase change specifically to a standard heat of vaporization and melting.

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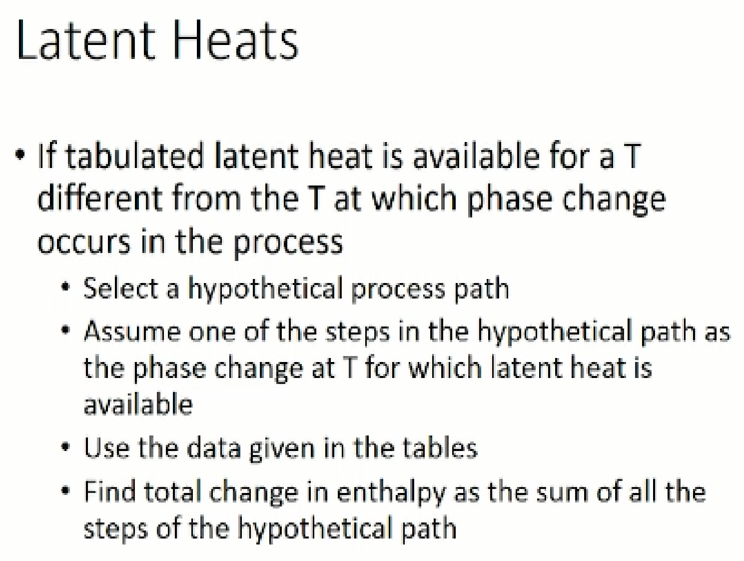

Latent Heats

- If tabulated latent heat is available for a T different from the T at which phase change occurs in the process
  - Select a hypothetical process path
  - Assume one of the steps in the hypothetical path as the phase change at T for which latent heat is available
  - Use the data given in the tables
  - Find total change in enthalpy as the sum of all the steps of the hypothetical path

As I was explaining what you do is you would want to use the tabulated latent heat which is available for specific temperatures and if the process itself is happening at a different temperature then you would build a hypothetical path. One of the steps in the hypothetical path would have to be the phase change at the temperature for which the latent heat is available. Then you can use the data given for that particular step.

And for the other steps which are the hypothetical steps in the process you would calculate the change enthalpy using either integral CPDT or v cap delta P or assuming it to be 0 and so on so depending on the type of process which is happening.

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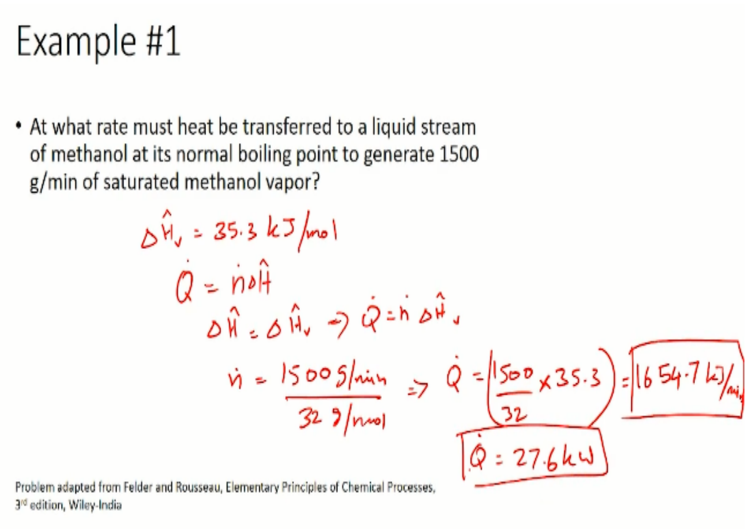

Example #1

- At what rate must heat be transferred to a liquid stream of methanol at its normal boiling point to generate 1500 g/min of saturated methanol vapor?

$$\Delta \hat{H}_v = 35.3\ kJ/mol$$

$$\dot{Q} = \dot{n}\Delta\hat{H}$$

$$\Delta\hat{H} = \Delta\hat{H}_v \Rightarrow \dot{Q} = \dot{n}\Delta\hat{H}_v$$

$$\dot{n} = \frac{1500\ g/min}{32\ g/mol} \Rightarrow \dot{Q} = \left(\frac{1500}{32} \times 35.3\right) = \boxed{1654.7\ kJ/min}$$

$$\boxed{\dot{Q} = 27.6\ kW}$$

Problem adapted from Felder and Rousseau, Elementary Principles of Chemical Processes, 3rd edition, Wiley-India

So, here is an example problem this is a very simple and straightforward example problem. You have been asked to calculate at what rate the heat must be transferred to a liquid stream of methanol at its normal boiling point to generate 1500 grams per minute of saturated methanol vapor. To calculate this, we need to know the heat of vaporization at its normal boiling point so normal boiling point would be the boiling point when pressure is 1 atmosphere.

The standard heat of vaporization for methanol at its boiling point is given to as delta H cap v which is the standard heat of vaporization=35.3 Kilojoules per mol. So, we have the mass flow rate for methanol we would have to convert that into molar flow rate and we can use this heat of vaporization to calculate the amount of heat required. So, this is an open system which would mean the equation for heat transfer would be Q dot = n dot delta of H cap.

So here delta H cap= delta H cap v because the only process happening is change in phase. So, Q dot =n dot times delta H cap v. So your n. can be calculated from the mass flow rate using the molecular weight. So Mass flow rate is 1500 grams per minute molecule weight of methanol is 32 grams per mol. So, this gives you n. so using this we can calculate Q dot as 1500/32 times the heat of vaporization which is 35.3.

The total value you end up with this 1654.7 kilojoules per minute. So this is the rate at which heat needs to be transferred for vaporizing 1500 grams per minute of methanol liquid to obtain saturated methanol vapor at its normal boiling point. So, this can also be converted to kilowatts by dividing it by 60 so kilowatts term would be 27.6 kilowatts. So, this is a simple calculation where we performed a very simple energy balance.

For a process where only phase change is happening. So, this is a very simple process because phase change happens here at constant temperature and constant pressure and this is also happening at the normal boiling point which means the heat of vaporization was directly available and all we needed to do was multiply this heat of standard heat of vaporization with molar flow rate to get the rate of heat transfer.

However usually in real scenarios problems are a little more complicated because the phase change might not be happening at its boiling point. So, then you would have to assume a hypothetical path which would make the problem a little more complicated.

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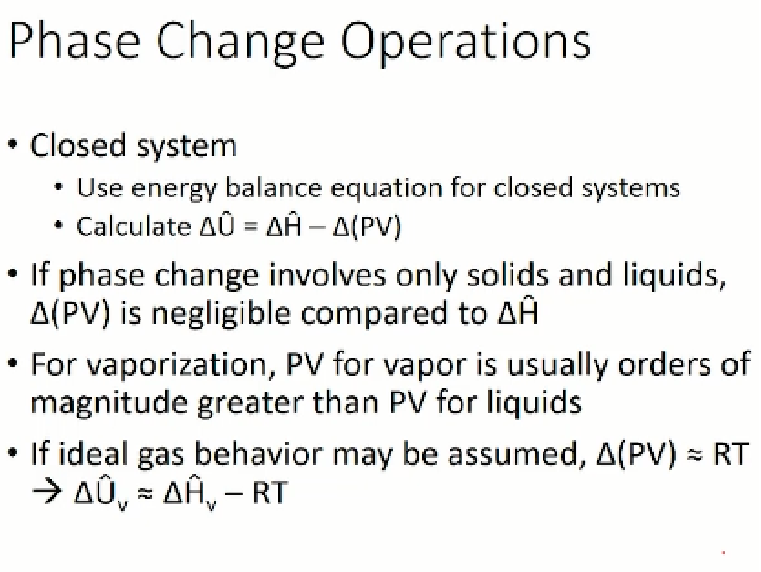

Phase Change Operations

- Closed system
  - Use energy balance equation for closed systems
  - Calculate $\Delta\hat{U} = \Delta\hat{H} - \Delta(PV)$
- If phase change involves only solids and liquids, $\Delta(PV)$ is negligible compared to $\Delta\hat{H}$
- For vaporization, PV for vapor is usually orders of magnitude greater than PV for liquids
- If ideal gas behavior may be assumed, $\Delta(PV) \approx RT$ $\rightarrow \Delta\hat{U}_v \approx \Delta\hat{H}_v - RT$

In the example problem we saw we had an open system and we were able to use the standard heat of vaporization directly. You could also have closed system where phase change might be happening in such a scenario you would have to use internal energy changes. So you can actually calculate internal energy changes as delta H cap-delta PV. If phase change involves only solids and liquids, then delta PV is usually negligible compared to the delta H cap.

This is because the specific volume of solids and liquids is very small and because of this the second term becomes small so and you can approximate change in internal energy to be equal to the change in specific enthalpy. However, if you have vaporization or condensation as a process where you have one of the phases being a vapor or gas then PV is usually orders of magnitude greater than PV for gas is orders of magnitude greater than the PV for liquids.

In which case you have to use this value so for ideal gases delta PV can be approximated to RT so delta U cap V can be calculated as delta H cap V – RT. This is an approximation however it is useful for performing calculations for phase change operations where one of the phases involved is a gas phase.

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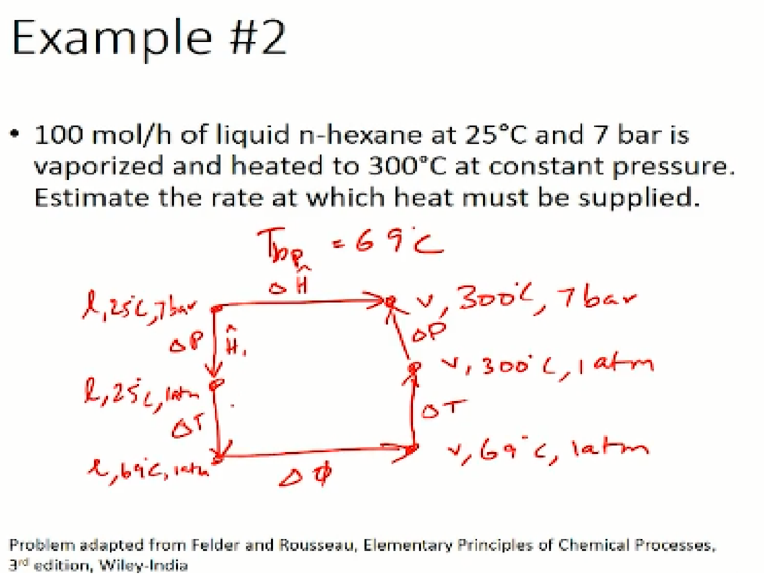

Example #2

- 100 mol/h of liquid n-hexane at 25°C and 7 bar is vaporized and heated to 300°C at constant pressure. Estimate the rate at which heat must be supplied.

Problem adapted from Felder and Rousseau, Elementary Principles of Chemical Processes, 3rd edition, Wiley-India

So here is a second example problem again its an open system where 100mols of liquid n hexane is coming in per hour at 25 degrees Celsius and 7 bar and is vaporized and heated to 300 degrees Celsius at constant pressure. You are asked to estimate the rate at which heat must be supplied. In the real process it is a constant pressure process where heating is happening from 25 degrees Celsius to 300 degrees Celsius.

So, in reality the phase change would be happening at a boiling point associated with 7 bar pressure. So, if you were to look up the vapor pressure charts the associated boiling point for n hexane at 7 bar would be 146 degrees Celsius however the heat of vaporization at 146 degrees

Celsius is not available for n hexane. We do have the value for heat of vaporization of n hexane at 1 bar and its normal boiling point.

So, the normal boiling point for n hexane is 69 degrees Celsius. So, we would have to assume a hypothetical part where phase change happens at this normal boiling point. So, first step is to identify a hypothetical path which can be constructed to perform the calculations. So, you have the initial state which is liquid 25 degree Celsius and 7 bar and the final state which is vapor 300 degree Celsius and 7 bar.

As we want the phase change to happen at one atmosphere let the first step of the hypothetical bar path be liquid at 25 degrees Celsius and 1 atmosphere. But only pressure is changing and the second step is where temperature is increased from 25 degrees Celsius to the boiling point. So it goes to liquid 69 degrees Celsius and 1 atmosphere. So here only temperatures changing and the next step is where the phase is changing.

So, it goes to vapor at 69 degree Celsius and 1 atmosphere so from here we can heated to vapor at 300 degree Celsius and 1 atmosphere and the last step of the hypothetical path is to change the pressure from 1 atmosphere to 7 atmosphere 7 bar. So, this hypothetical path has 1234 and 5 steps instead of the single step which is the real path. So, each of these steps in the hypothetical path have been constructed in aware that either pressure temperature or the phase are changing.

Not more than one of these 3 changes in any of the steps which means we would be able to calculate the change in specific enthalpy for each of these steps. So, the total specific enthalpy change can be calculated as delta H cap. So, far which would have the calculate H1 cap H2 cap H3 cap H4 cap and H5 cap and find summation of this.

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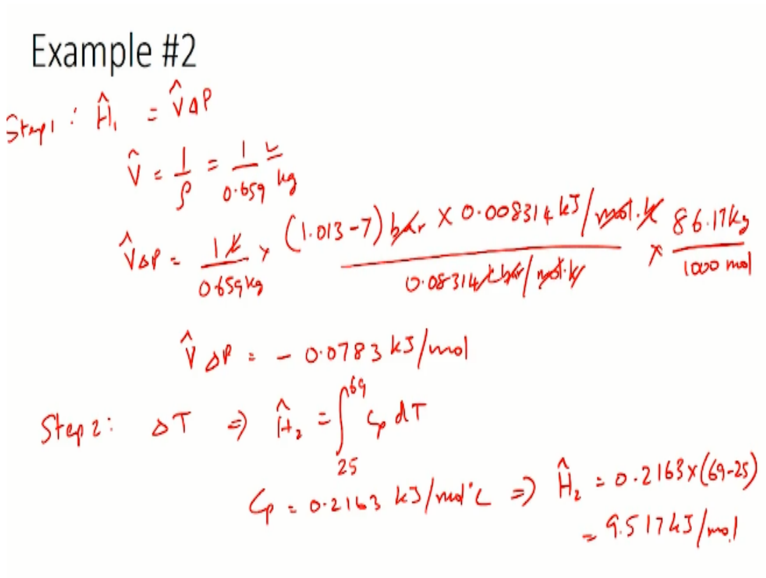

Example #2

Step1 : $\hat{H}_1 = \hat{V}\Delta P$

$$\hat{V} = \frac{1}{\rho} = \frac{1}{0.659}\,\frac{L}{kg}$$

$$\hat{V}\Delta P = \frac{1\cancel{L}}{0.659\,kg} \times \frac{(1.013-7)\,\cancel{bar} \times 0.008314\,kJ/\cancel{mol.K}}{0.08314\,\cancel{L}\,\cancel{bar}/\cancel{mol.K}} \times \frac{86.17\,kg}{1000\,mol}$$

$$\hat{V}\Delta P = -0.0783\,kJ/mol$$

Step 2: $\Delta T \Rightarrow \hat{H}_2 = \int_{25}^{69} C_p\,dT$

$$C_p = 0.2163\,kJ/mol^{\circ}C \Rightarrow \hat{H}_2 = 0.2163\times(69-25) = 9.517\,kJ/mol$$

So let us first calculate the change in enthalpy for the first step which is H1 cap. So, this would be = v cap delta P because there is a change in pressure for a liquid phase system. So, we can calculate v cap using the density values for n hexane v cap would be 1/density so the density from the tables can be identified as 0.659 and 1/0.659 is the v cap value and now we have to calculate v cap delta p.

So, we kept the would be 1/0.659 times delta P which is 1.013–7 bar and this bar needs to be converted into units which would be recognizable for cap value v cap in terms of liters per kilogram. So this is liters per kilogram so for this conversion we can use the R value in terms of SI value units and R value in terms of bar which would be 0.008314 kilojoules for mol kelvin/ 0.08314 liter bar mol Kelvin.

So, mol kelvin will get cancelled off bar will get cancelled off so liters get cancelled off here and we end up with v cap delta P in terms of kilojoules per kilogram as hexane flow rate has been given in terms of mols it would be useful to convert these kilojoules per kilogram* kilojoules per mol. So, we can use the molecular weight and multiply the molecular weight which is 86 .17 per kilo grams per kilo mol which is 1000 mols.

So, from here we would be able to get v cap delta p as - 0.0783 kilojoules per mol. So, this is the first step the second step so the second step would have to be calculated so for the second step there is delta T and there is no change in pressure or phase so this is a simple thing so H2 cap would be = integral CpdT where Cp would be the Cp of hexane liquid and the temperature differences from 25 degree Celsius to 69 degrees Celsius.

So, Cp for n hexane liquid is 0.2163 kilojoules per mol degree Celsius. So, your H2 cap would be = 0.2163 times 69–25 which is 9.517 kilojoules per mol.

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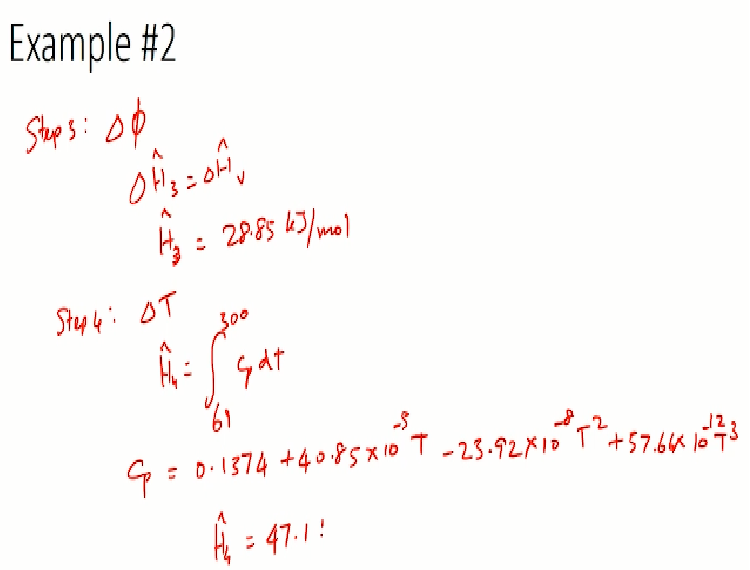

Example #2

Step 3: $\Delta\phi$

$$\Delta\hat{H}_3 = \Delta\hat{H}_v$$

$$\hat{H}_3 = 28.85 \text{ kJ/mol}$$

Step 4: ΔT

$$\hat{H}_4 = \int_{61}^{300} C_p\, dt$$

$$C_p = 0.1374 + 40.85\times10^{-5}T - 23.92\times10^{-8}T^2 + 57.66\times10^{-12}T^3$$

$$\hat{H}_4 = 47.1!$$

So, the step 3 for the process is change in phase. So, here the phase changes are happening at normal boiling point so we can use the heat of vaporization directly delta H3 cap= delta Hv cap so H3 cap is basically=28.85 kilojoules per mol and this is a value you look up the tables. So, there are tables available for getting this value on in your textbooks and also in other hand books. Table B1 in your Felder Rousseau textbook actually gives the change in specific enthalpy.

For phase change process which is called as the heat of vaporization and heat of melting. So, now the step 4 which is delta T where only temperature changes and phase and pressure are a constant H4 cap is integral CpdT however here it would be the Cp of hexane vapor and the temperature increases from 69 to 300 degrees Celsius. So, you can get the Cp value from the tables or from some handbook.

So, this would be 0.1374+40.85 times 10 power -5 T- 23.92 times 10 power -8T square+ 57.66

times 10 power – 12 cube so this would be in terms of kilojoules per mol degree Celsius. So, integrating this equation with the limits of 69 and 300 you would get H4 cap as 47.1 kilojoules per mol.

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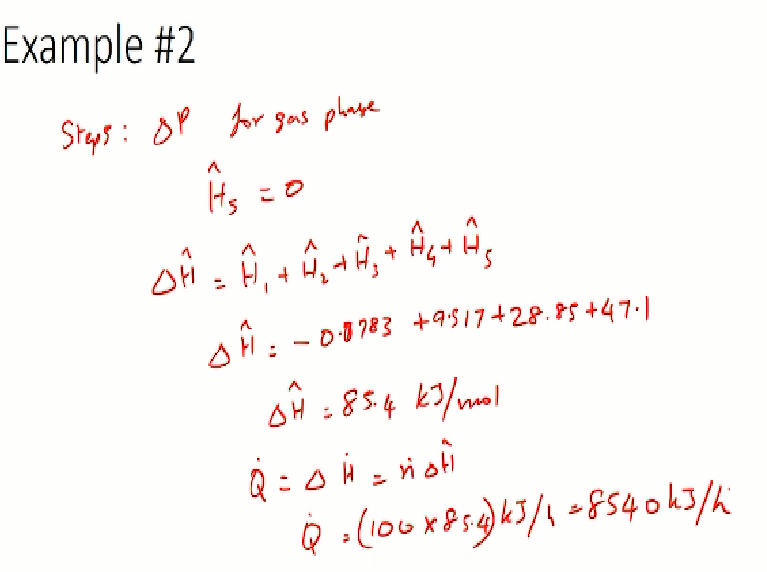

Example #2

Steps: ΔP for gas phase

$$\hat{H}_5 = 0$$

$$\Delta\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_3 + \hat{H}_4 + \hat{H}_5$$

$$\Delta\hat{H} = -0.0783 + 9.517 + 28.85 + 47.1$$

$$\Delta\hat{H} = 85.4 \text{ kJ/mol}$$

$$\dot{Q} = \Delta\dot{H} = \dot{n}\Delta\hat{H}$$

$$\dot{Q} = (100 \times 85.4) \text{ kJ/h} = 8540 \text{ kJ/h}$$

So, the last step for the process is delta P which is the step 5. So, this delta P is happening for gas phase assuming ideal gas behavior H5 cap=0. Because we know that change in enthalpy for constant temperature processes where only pressure changes is 0 for ideal gases. So, using that we can ignore the last step. So, total H cap= H1 cap + H2 cap+ H3 cap+ H4 cap+ H5 cap. So we have the numerical values for all of them using that.

We can calculate delta H cap as – 0.0783+9.517+28.85+47.1 giving you delta H cap as 85.4 kilojoules per mol. So, from here we can calculate H dot which would be = Q dot Q dot= delta H dot = n dot delta H cap. So n. has been given as 100mols and from there we can calculate Q dot = 100 times 85.4 kilojoules per hour= 8540 kilo joules per hour. So, in this calculation one thing you would have seen is the first step which is v cap delta P.

The change in enthalpy P due to a change in pressure for the liquid was very small compared to all other enthalpy changes. We had 4 processes where we had accounted for change in enthalpy and in the last one we have assumed ideal gas behavior and calculated the changed enthalpy to be 0. So for the first process where you had change in pressure for a liquid we had calculated v cap delta P the numerical value for that was –0.0783.

And every other value you had was orders of magnitude higher than this value indicating that how insignificant this particular step can be. So, because of this in some cases it is okay to assume that this change in enthalpy due to change in pressure even for liquids or solids can be 0 unless the change in pressure is very very large. So, with that we come to the conclusion for todays lecture in tomorrows lecture we will talk about how to estimate this heat of vaporization.

I just had used values which I said I picked up from tables so these values are experimentally measured. H however if some values are not available to you how can you actually get that out. There are some correlations which can be used we will look at how these correlations can be used to arrive at the answers until then thank you and goodbye.